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(54) Title: PROTECTIVE LAYERS FOR SPUTTER COATED ARTICLE

(57) Abstract: Tin is added to a zinc cathode target to enhance the sputter efficiency of the target. Films deposited using the cathode, e.g., greater than zero but less than 10 weight percent tin and greater than 90 but less than 100 weight percent zinc improve the chemical durability of a high transmittance, low emissivity coating stack over coating stacks having zinc oxides without tin oxide. High transmittance, low emissivity coating stacks are heated with the heated coating having reduced haze by selecting the thickness of metal primer layer between an infrared reflective film, e.g. a silver film and a dielectric film, e.g., a 52-48 zinc stannate, zinc oxide, tin oxide film or a zinc oxide film. Also disclosed are enhancing films that lower the resistivity of silver films deposited thereon and improve chemical durability of the coating stack.

PROTECTIVE LAYERS FOR SPUTTER COATED ARTICLE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation in part  
5 application of Application Serial Nos. 09/302,409, filed April  
30, 1999.

FIELD OF THE INVENTION

This invention relates, in general, to protective  
10 layers for sputter coated articles such as coated or uncoated  
glass or transparent. Such articles with the protective  
layers are shippable, heat treatable, can have low emissivity  
coating or coatings. The invention also relates to the coated  
articles and to methods of making the coated articles.

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DISCUSSION OF THE PRESENTLY AVAILABLE TECHNOLOGY

U.S. Patent No. 4,610,771 ("U.S.P.N. '771")  
discloses an antireflective sputtered metal oxide film  
deposited using a zinc/tin alloy target. U.S.P.N. '771 in  
20 column 3, line 26, to column 4, line 12, discusses the use of  
the alloy target to deposit a zinc stannate film having, in  
general, oxides of zinc and tin preferably in proportions of  
10 to 90 percent zinc and 90 to 10 percent tin.

Although the zinc/tin alloy target disclosed in  
25 U.S.P.N. '771 to deposit the zinc stannate film is acceptable,  
there are limitations. More particularly, in a low E coating  
such as the type described in U.S.P.N. '771, an infrared  
reflecting metal film or layer, e.g., silver is deposited on  
the zinc stannate film. A silver film deposited on a  
30 sputtered zinc stannate film has a higher electrical  
resistivity and higher emissivity than a silver film deposited  
on a sputtered zinc oxide film or layer. More particularly,  
U.S. Patent No. 5,821,001 ("U.S.P.N. '001") discloses a silver  
film deposited on a zinc oxide film; the atoms of the silver  
35 film deposit in a form characterized by a low electrical  
resistivity which provides the silver film with a low  
emissivity. In depositing the zinc oxide film the process

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parameters are selected to deposit a zinc oxide layer with a suitable crystallinity or preferential crystal growth for favorably affecting deposition of the silver atoms of the silver film.

5           Sputtering zinc in a reactive atmosphere, e.g., oxygen, to provide a zinc oxide film over which a silver film having a low electrical resistivity is deposited has drawbacks. For example, it is difficult to reactively sputter a pure zinc target, i.e., a target of about 100% zinc metal,  
10   in a reactive atmosphere such as oxygen for reasons discussed in more detail below.

U.S.P.N. '001 also discloses a heat treatable low emissivity film. The thickness of the primer layers, e.g., titanium films, may be increased to provide enhanced  
15   mechanical durability, i.e., improve shear resistance. The shear resistance test consists of applying 20 successive strokes of a cloth wetted with deionized water against the coated surface of glass, followed by visual examination of the tested area. Depending on the appearance of the tested area,  
20   letter grades of D-, D, D+...A, A+ are assigned to the coating; then, for numerical analysis, assignments of 5 to D-, 10 to D, 55 to A, and 60 to A+ are made. If a coating shows no signs of shear, not even barely visible scratches, then it receives a maximum rating of 60. Coatings that display  
25   uniform shear and delamination at any interface of the multi-layer coating within the test area receive a failing rating of zero. Other levels of performance receive intermediate scores. This method of coating durability characterization has been found to correlate well with field performance of the  
30   coating. The drawback with using thick primer layers is that the coating stack after heating, e.g., glass tempering or glass bending operations, is likely to have a hazy appearance when viewed using a dark room, flood-light haze test. In the dark room, floodlight haze test, the coated specimen is viewed  
35   in reflection in a dark room at various viewing angles relative to a spotlight, in order to find the geometry yielding maximum scattering of light, or, in other words,

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haze, possible from the coating. If there is no geometry that can make haze observable, an A+ rating is assigned to the sample. Very poor samples receive D-. For purposes of numerical analysis, the letter grades are given values of 5 to 60, as described above for the shear test. Lower haze corresponds to higher numerical values.

As can be appreciated by those skilled in the art of making sputtered coatings, it would be advantageous to provide a zinc target that may be sputtered in a reactive atmosphere without the drawbacks of the presently available zinc targets and to provide low emissivity coated articles that have mechanical durability so that the coated article may be shipped and subsequently heated without the heated coating having haze.

The disclosures of U.S.P.N.'s '771 and '001 are hereby incorporated in toto by reference.

#### SUMMARY OF THE INVENTION

This invention relates to a sputter cathode target having tin preferably in an amount greater than zero and less than 10 weight percent of the total weight of the target material, and zinc in an amount preferably less than 100 weight percent and more than 90 weight percent of the total weight of the target material. Hereafter, unless indicated otherwise, the term "weight percent" means the weight percent of the total weight of the target material.

As used herein, "a zinc stannate film," e.g., of the type discussed in U.S.P.N. '771 is an oxide of an alloy of zinc and tin. The cathode used is made of an alloy of zinc and tin. A "zinc oxide, tin oxide film," is a film having oxides of tin and zinc. The cathode used to sputter the zinc oxide, tin oxide film is made of zinc having additions of tin as is discussed in detail below.

In one embodiment of the invention a coating stack has a zinc stannate film deposited on a glass substrate, a zinc oxide, tin oxide film deposited on the zinc stannate film; an infrared reflecting film, e.g., silver, deposited on

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the zinc oxide, tin oxide film; a primer layer, e.g., a titanium metal film, deposited on the infrared reflecting film; a zinc oxide, tin oxide film deposited on the primer film, a zinc stannate film deposited on the zinc oxide, tin oxide film; an infrared reflecting film deposited on the zinc stannate film; a primer layer deposited on the infrared reflecting layer; a zinc oxide, tin oxide film deposited on the primer layer, a zinc stannate film deposited on the zinc oxide, tin oxide film; and a protective layer, e.g., a titanium metal film and/or a titanium oxide film in either order, deposited over the zinc stannate film. In another embodiment of the invention, a zinc oxide film is used in place of the zinc oxide, tin oxide film. In a further embodiment of the invention, a zinc stannate film is used in place of the zinc oxide, tin oxide film. When a zinc stannate film is used in place of the zinc oxide, tin oxide film, the zinc stannate films differ in composition by at least 5 weight percent. For example, when one of the zinc stannate films is about 50 weight percent zinc and 50 weight percent tin, the other zinc stannate film is about 10-45 or 55-90 weight percent zinc and 55-90 or 45-10 weight percent tin. In a still further embodiment of the invention, a first deposited zinc stannate film is  $50 \pm 10$  weight percent zinc and  $50 \pm 10$  weight percent tin. The second deposited or overlying zinc stannate film has tin equal to or greater than 10 weight percent and less than 40 weight percent and preferably 20 weight percent, and has zinc equal to or less than 90 weight percent and greater than 60 weight percent and preferably 80 weight percent. Overlying zinc stannate films having 90 weight percent zinc and 10 weight percent tin have been used.

Another aspect of the present invention is the composition or films of the protective layer. Of course, the protective layer can be for any multi-layered stack with one or more antireflective layers on a substrate. This multi-layered stack has at least one layer of at least one infrared reflecting film which can be preceded on the near side towards the substrate by one or more dielectric and/or zinc- and/or

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tin-containing films and can be followed on the side away from the substrate by one or more layers of one or more dielectric and/or zinc- and/or tin-containing films and/or a primer layer. This is also the type of multi-layered stack for the protective layer. Any zinc- and/or tin-containing films can be zinc oxides or tin oxides or the zinc stannates like those in Patents '771 and '001. The protective layer is either a metal film or silicon film or metal oxy-material film or silicon oxy-material film or both. The metal oxy-material or silicon oxy-material film is either or both metal oxide or silicon oxides films or metal oxynitride or silicon oxynitride films. These metal, metal oxide and metal oxynitride films have one or more metals that are the same or different from metal film to metal oxide or oxynitride film where the metals are those transition metals of Groups, 4, 5, and 10 of the Periodic Table of Elements for the Revised Chemical Element Group Notation having upto 18 groups and alloys thereof that are capable of being sputtered coated. For the protective layer the order can be metal film and metal oxide or oxynitride film or the reverse. The protective layer can be the outermost layer on the multi-layered stack but it only needs to be in a position in the multi-layered stack where it can perform the protective function for providing some chemical and/or mechanical durability to the multi-layered stack. Hence there can be additional film or coating layers over the protective layer if desired.

The above-described coating stack has mechanical and chemical durability. The coatings of the instant invention in addition to having mechanical and chemical durability which make them acceptable for shipment can be heat treated with the heat treated coating having reduced haze. The reduction in haze after heating is accomplished by selecting metal primer thicknesses which is discussed below. The procedure for determining haze was discussed above. As used herein a reduction in haze is a numerical increase of about 10. An advantage of the coatings of the instant invention is that a coating of the invention may be deposited on a substrate, the

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coated substrate shipped to a fabricating facility where the coated substrate is heat-treated, e.g., heated to temperatures up to about 1350°F (732°C). The coating of the invention has particular application in the making of solar control  
5 automotive windshields. Sheets of glass having a low emissivity coating of the invention are coated in one facility and then shipped to another facility where the coated glass sheet is processed, e.g., into an automobile windshield.

#### 10 DISCUSSION OF THE INVENTION

For a full appreciation of the various embodiments of the invention, the embodiments will be discussed separately and then combined. The first embodiment of the invention to be discussed is the use of a zinc cathode having low amounts  
15 of tin to improve the deposition of zinc oxide films and the benefits of a zinc oxide film having low amounts of tin.

The embodiments of the invention relating to zinc sputtering target having low amounts of tin and to a method of reactively sputtering such zinc targets to sputter deposit a  
20 zinc oxide, tin oxide film will be discussed. As will be appreciated, the invention contemplates using the target of the instant invention to deposit a zinc oxide, tin oxide film over or under an infrared reflective film, e.g., gold, silver or aluminum film, other metal films, e.g., primer films such  
25 as a titanium metal, or ceramic films, or other dielectric films.

The sputtering cathode target in one embodiment of the invention has greater than zero weight percent and less than 10 weight percent tin, and less than 100 weight percent  
30 and more than 90 weight percent zinc to improve the emissivity of an infrared reflective film, e.g., a silver film, deposited on the zinc oxide, tin oxide film and to improve the sputtering of the zinc cathode target having low amounts of tin. The cathode target of the instant invention may also be  
35 defined as having greater than 0 and less than 10 weight percent tin with the majority of the balance zinc, or as having less than 100 weight percent and more than 90 weight

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percent zinc with the majority of the balance tin. Before discussing this embodiment of the invention, the drawbacks and/or limitations of reactively sputtering a zinc cathode target without tin and limitations of zinc oxide films,

5 deposited using such cathodes are discussed for a better appreciation of the invention.

Typically, a metal target is reactively sputtered in a gas such as oxygen, or gas mixture of oxygen with other gases such as nitrogen, argon or helium. Sputtering in a gas  
10 mixture will result in a higher sputtering rate for a stable process but requires more control to maintain the process stability, e.g., requires controlling flow rate of two gases. Because of the higher sputtering rate, it is preferred to sputter in a gas mixture rather than in oxygen alone. In  
15 either case the resulting coating is a metal oxide, e.g., zinc oxide when a zinc target is used.

Zinc oxide is a common dielectric material that is used as a high refractive index film in coating stacks having low emissivity. In the flat glass industry these coatings are  
20 usually applied by horizontal vacuum coaters using high power supplied from a direct current source to energize cathodes that sputter layers onto glass substrates. Higher coater throughput requires higher power density to the cathode target. This in turn increases the tendency for the targets  
25 to arc, particularly during reactive sputtering.

During reactive sputtering the frequency of arcing of the zinc cathode target increases with time, and debris in the form of powder and flakes builds up on the target surface and adjacent areas. Debris in the form of powders, flakes and  
30 splatter eventually falls onto the surface of the substrate being coated resulting in unacceptable coated product. Further the arcing increases to a point where the process becomes unstable. In addition, areas of the target surface have a tendency to blacken over time. These blackened areas  
35 are nonconductive, thus limiting the sputtering rate and leading to non-uniformity in the coating.



The arcing and debris buildup to some degree may be reduced by periodic sputter cleaning as is known by those skilled in the art of sputter coating. One technique for sputter cleaning is to periodically sputter the targets for a certain time period in an inert gas, such as argon or helium, which sputters the target as a metal. Sputter cleaning to some degree removes the oxide buildup on the target surface that causes arcing. The black areas on the target may not be reduced by sputter cleaning. The debris and arcing, however, continually degrade the target, and after a period of time, the coater downtime increases and, consequently, there is less production time for the coater. Zinc targets because of their tendency to frequently arc during sputtering are difficult to sputter clean and require longer and more frequent cleaning.

In the practice of the invention, tin is added to a zinc target to reduce if not eliminate the above drawbacks, e.g., reduce the amount of flaking debris, reduce powdery buildup on the target, minimize arcing, and minimize, if not eliminate, blackening of the target surface areas. The amount of debris and degrading of the zinc target of the instant invention is considerably less with time than for a pure zinc target. As a result, less periodic target cleaning is required with less duration of the cleaning in an inert gas.

As previously discussed, U.S.P.N. '771 discloses a zinc-tin alloy target to deposit a zinc stannate film, i.e., an oxide of a zinc tin alloy having 10 to 90 weight percent zinc and 90-10 weight percent tin. The zinc-tin alloy cathode target of U.S.P.N. '771 provides a zinc stannate film that has better chemical durability than a zinc oxide film. Further, the zinc-tin alloy cathode target has less arcing and minimal debris buildup, e.g., there is no measurable powder buildup. As is well-known in the art of sputter coating, zinc oxide films readily dissolve in acid and base solutions; zinc stannate films have reduced solubility in acid or base.

Although the properties of the zinc oxide, tin oxide film of the instant invention have not been studied in great detail, it is believed that the following will occur. As the

tin approaches zero weight percent, the chemical durability of the deposited film decreases, and the problems associated with sputtering a zinc target in a reactive atmosphere increase. As the weight percent of tin approaches ten, the chemical durability of the zinc oxide film increases, and the problems associated with sputtering a zinc target in a reactive atmosphere decrease. The electrical resistivity of a silver film deposited on the zinc oxide, tin oxide film is expected to be similar to a silver film deposited on a zinc oxide film.

10 In the practice of this embodiment of the invention, a zinc target having tin greater than zero and less than ten weight percent is a useable range; 0.5 to 9.5 weight percent of tin is a practical range; 4 to 8.5 weight percent of tin is a preferred range, and 5 to 9.5 weight percent of tin is a more preferred range. The weight percent of tin and zinc in a zinc oxide, tin oxide film is expected to be similar to the weight percent of zinc and tin in the target.

As can now be appreciated, as the weight percent of tin in the zinc cathode increases, the chemical durability of the deposited film is expected to increase. Further, the crystalline structure of the zinc oxide film having tin in weight percents greater than zero and less than ten is similar if not identical to the crystalline structure of zinc oxide film having zero weight percent of tin. Further, a zinc stannate film having 60-90 weight percent zinc and 10-40 weight percent tin have similar crystalline structures as zinc oxide. Therefore, it is expected that emissivity of silver film deposited on a zinc oxide film will be similar to a silver film deposited on a zinc stannate film having 60-90 weight percent zinc and 10-40 weight percent tin. At values of less than 60 weight percent zinc, the crystalline structure starts to change and the emissivity and resistivity start to increase. Transmission Electron Microscopy has shown a weak zinc oxide electron diffraction pattern for a zinc stannate film having 66 weight percent zinc and 34 weight percent tin, and an amorphous structure for zinc stannate film having 47 weight percent zinc and 53 weight percent tin.

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The coated articles disclosed in U.S.P.N. '001 and U.S. Patent Application Serial No. 09/023,746 filed February 13, 1998, in the names of Mehran Arbab, Russell C. Criss, Gary J. Marietti and Paul A. Medwick for "Coated Articles" (hereinafter "U.S.P.A. No. 09/023,746") may be made practicing this embodiment of the instant invention which includes but is not limited to sputtering a cathode target having 92 weight percent zinc and 8 weight percent tin in an atmosphere having more than 75% oxygen and the remainder argon. Further, problems discussed above associated with sputtering a zinc target are expected to be minimized if not eliminated.

The discussion will now be directed to improving chemical durability of the coating stack, reduction of haze of the coating stack and decreased emissivity of the infrared reflective metal, e.g., silver. "Chemical durability" means the coating is not readily attacked by acid or base solutions. Reference may be had to U.S.P.N.'s. '001 and '771 for a discussion on chemical durability. The test for haze was discussed above.

From the above discussion, the emissivity of the silver film may be reduced by depositing the silver layer on a zinc oxide film; a zinc oxide, tin oxide film or a zinc stannate film having zinc in the range of 60 to 90 weight percent and tin in the range of 10 to 40 weight percent. Further, from the above discussion, chemical durability of a layer having a zinc oxide film under a silver film and over a zinc stannate film may be enhanced by adding tin to a zinc target to provide a zinc oxide, tin oxide film, or a zinc stannate film. As used herein, "a chemical and electrical enhancement film" is a zinc oxide, tin oxide film and/or a zinc stannate film having zinc in the range of 60 to 90 weight percent and tin in the range of 10 to 40 weight percent. The chemical and electrical enhancement film of the invention may be used in place of zinc oxide films to enhance chemical durability of the coating stack while obtaining a silver film having low emissivity. By way of illustration, coated

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articles having a glass substrate/zinc stannate film/zinc oxide film/silver film/titanium metal primer film/zinc oxide film/zinc stannate film/zinc oxide film/zinc stannate film/titanium metal and/or titanium oxide or oxynitride  
5 protective overcoat may be chemically enhanced by using the chemical and electrical enhancement film of the invention for one or more or all of the zinc oxide film(s) of the above coating stack.

Another coated article includes glass substrate/zinc  
10 stannate film/zinc oxide film/silver film/titanium metal primer film/zinc oxide film/zinc stannate film/titanium metal and/or titanium oxide or oxynitride protective overcoat. As can now be appreciated, the chemical and electrical enhancement film of the invention may be substituted for one  
15 or more or all of the zinc oxide film(s) of the above coating.

In the practice of the instant invention, a dielectric layer may include a zinc stannate film, and a chemical and electrical enhancement film. Where the chemical and electrical enhancement film is zinc stannate, the  
20 difference between the composition of the zinc stannate film and the zinc stannate film of the chemical and electrical enhancement film is at least 5 weight percent zinc. For example, and not limiting to the invention a zinc stannate film having 58 weight percent zinc and 42 weight percent tin  
25 may be used with a zinc stannate film (chemical and electrical enhancement film) having 63 to 90 weight percent zinc and 10 to 37 weight percent tin.

The discussion will now be directed to the embodiment of the invention to provide a coating stack that is  
30 chemically and mechanically durable and a coating stack that has reduced haze after subjecting the coating stack to elevated temperatures, e.g., but not limiting to the invention, above room temperature and below about 1350°F (732°C). As will be appreciated by those skilled in the art,  
35 the invention is not limited to the coatings discussed below which are presented for illustration purposes only. The following Table 1 provides a few embodiments of coating stacks

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that may be used in the practice of the invention; however, as will be appreciated, the invention is not limited thereto.

TABLE 1

Coating Samples	Substrate	FILM													
		1	2	3	4	5	6	7	8	9	10	11	12	13	
1	X	X	X	X	X		X						X		
2	X	X	X	X	X		X		X	X		X	X		
3	X	X		X	X	X	X		X	X		X	X		
4	X	X		X	X		X		X	X	X	X	X		
5	X	X	X	X	X	X	X		X	X		X	X		
6	X	X	X	X	X		X		X	X	X	X	X		
7	X	X		X	X	X	X		X	X	X	X	X		
8	X	X	X	X	X	X	X		X	X	X	X	X		
9	X	X	X	X	X	X	X	X	X	X	X	X	X		
10	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
11	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
12	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
13	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Layers		A	B	C	D	E	F	G	H	I	J	K	L	M	

5

The second column from the left is entitled "Substrate." The material of the substrate is not limiting to the invention and may be made of any material, e.g., glass, fiberglass, plastic, metal, wood or ceramic. The type of articles that are made in the preferred practice of the invention are transparencies for residential and commercial buildings, and land, air, space, above, on and below water vehicles, therefore, the substrate is preferably transparent and made of glass, and flexible and rigid plastics. Glass when used may be clear or tinted and made by any process including the float glass manufacturing process, and the type of glass is not limiting to the invention. It is expected that the coated article will be subjected to elevated temperatures; therefore, the substrate selected should be able to withstand the elevated temperatures. In our discussion, but not limiting to the invention, the substrates are glass sheets or pieces.

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The columns numbered 1-13 are films, and the columns labeled A-H are layers, of coating stacks that incorporate

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features of the invention. The layers (see the bottom of the Table 1) include at least one film and as shown in the Table 1 up to 3 films. The layers A, D and G are dielectric layers. The index of refraction of the dielectric films of the layers A, D and G is preferably greater than the index of refraction of the transparent substrate to anti-reflect the infrared reflection layer. The invention is not limited to the type of dielectric films that may be used in combination with the chemical and electrical enhancement film of the invention.

Dielectric films that may be used in the practice of the invention include but are not limited to zinc oxide, tin oxide, silicon oxide, silicon nitride, and silicon oxynitride. It is preferred that films 1, 6 and 11 of the layers A, D and G, respectively are each a zinc stannate film having 52 weight percent zinc and 48 weight percent tin. The films 2, 5 and 7, and 10 of the layers A, D and G respectively may be a zinc oxide film, or a chemical and electrical enhancement film of the invention. Coating examples 12-13 of Table 1 are prophetic examples, but these coating examples show the presence of one or both of films 12 and/or 13 as layer H. Coating examples 12 and 13 are those with the least number of films which can have either or both of the protective films for the protective layer. Of course any of the other coating examples 2-8 can also have either or both for the H layer.

In the following discussion, the substrate is soda-lime-silicate clear glass and has an index of refraction about 1.5. As is known in the art, varying the thickness of the film and layers changes the color of the coated article, or may provide a coating with a neutral color. It is expected that in the practice of the invention, the dielectric layers and/or films have a thickness in the range of  $600 \pm 500$  Angstroms. The thickness of the zinc oxide film or the chemical and electrical enhancement film should be sufficient to affect the crystal structure of the silver film to be deposited thereon.

The films 3 and 8 of layers B and E, respectively, are infrared reflecting films and may be of any material that

reflects infrared energy, e.g., but not limiting to gold, silver and aluminum. In the practice of the invention silver is preferred. The thickness of the silver is not limiting to the invention and is selected to provide a transparent coating  
5 having low emissivity. Silver films having a thickness of  $200 \pm 150 \text{ \AA}$  and preferably  $100 \pm 25 \text{ \AA}$  may be used in the practice of the invention.

The films 4 and 9 of the layers C and F, respectively, are primer films which have the function of  
10 (1) protecting the infrared metal layer from oxidizing during sputtering of the dielectric films, (2) protecting the infrared reflecting layer during high temperature processing, (3) reducing haze formation in the coating stack during heating, and/or (4) providing the coating stack with  
15 mechanical durability for shipping the coated article. Primer films may be any of the type known in the art, e.g., metals such as titanium or ceramic, of the type disclosed in U.S. Patent Application Serial No. 09/215,560, filed December 8, 1998, the disclosure of which is hereby incorporated by  
20 reference. In the practice of the invention, the primer layer is preferably titanium.

Films 12 and 13 of the layer H is or are protective films to provide additional chemical and mechanical durability for the coating stack during shipping and storage. The  
25 protective films are thin film sputter coating of metals or silicon and metal or silicon oxy-materials where the metals and metal oxy-materials that may be used can be titanium, titanium dioxide, titanium oxynitride, zirconium, zirconium oxides, zirconium oxynitrides, niobium, niobium oxides,  
30 niobium oxynitrides, tantalum, tantalum oxide, tantalum oxynitride, chromium, chromic oxides, chromic oxynitrides, nickel oxide and/or oxynitrides, and silicon oxide, silicon dioxide, silicon aluminum nitride and alloys, combinations or mixtures of any two or more of these including those like  
35 nickel chromium, silicon chromium, silicon chromium nickel, and silicon nickel. Also the aforementioned oxides can be oxynitrides. The aforementioned metals are useful as single

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films for the protective layer at numerous locations in a stack of layers when the stack of films is heat treated and the metals are converted by the heat to metal oxide films or metal oxynitride films. The temperature of heating are those usually encountered in tempering and heating a substrate for shape-changing. When both the metal and the metal oxymaterial films are used either may be deposited first for the protective layer with the other film over the first deposited film for layer H. Generally the thickness of the films are for the metal film about 5 to about 60 Angstroms ( $\text{\AA}$ ), preferably about 10 to about 30  $\text{\AA}$  and most preferably 15 to 25  $\text{\AA}$ . The metal oxy film can have a thickness in the range from about 20 to about 50  $\text{\AA}$ , preferably 30 to 40  $\text{\AA}$ . Further, more than one protective film may be used. For example, but not limiting to the invention, a zinc oxide film over a titanium dioxide film may be used. The thickness of the Layer H is not limiting to the invention; however, the thickness should be thick enough to provide protection. The metal, metal oxy films can be deposited by any method known to those skilled in the art. Also part of the metal film can be oxidized by heating rather than depositing a separate metal oxide film.

Before discussing in detail the Samples of the Table 1, the following background information is provided for a better appreciate of the invention.

Using zinc oxide film, as discussed above, provides a silver layer having resistivity and emissivity lower than a silver layer deposited on a zinc stannate layer having less than about 60 weight percent zinc and more than about 40 weight percent tin.

U.S.P.N. '001 discusses increasing the thickness of the primer layer to enhance the mechanical durability of the coated article to make the coated article shippable. More particularly, U.S.P.N. 001 discloses that it has been found that where the coated article will be exposed to heat treatment during its production, there is a point at which the primer layer may be made either too thin or too thick. Too thin a primer layer results in a lack of protection for the



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reflective, metallic film from oxidation at high temperature thus rendering the coated article unacceptable for heat treatment and in poor shear resistance which makes the article unsuitable for long distance shipment for later thermal processing. Too thick a primer layer results in the formation of an undesirable haze in the coated article after heat treatment, also rendering it unacceptable for heat treatment. However, a limitation is that these films after heating have haze.

10           It has been determined that by selecting dielectric films and primer layers that a coating stack can be made that has reduced haze after heating. For coated articles that are shipped but not heated, the primer layer should be thick enough to protect the silver during deposition of the  
15   overlying dielectric film or layer on the silver layer. A thickness of primer layers in the range of about 8 to 12 Angstroms is sufficient. The thickness of the primer layer is increased when the primer layer is to protect the silver during heating of the coated article. A thickness of about 20  
20    $\pm 5\text{\AA}$  is acceptable.

For a coated article that is shippable and heatable with reduced haze, the thickness of the primer film is adjusted to compliment the dielectric layer or film arrangement. In accordance with the teachings of the  
25   invention, primer layer thickness in the range of 18-32 Angstroms ( $\text{\AA}$ ) and preferably 18-40 $\text{\AA}$  is acceptable to provide a coating stack with reduced haze after heating. The following Examples illustrate the invention.

In the following discussion, the thickness of the  
30   metal primer layer is as deposited. As can be appreciated, the thickness increases after heating, changing a portion of the titanium metal primer film to titanium oxide. A method that will be referred to as the "XRF Method" is discussed in U.S.P.N. '001. In general the XRF Method is used to measure  
35   the thickness of metal layers. The XRF Method uses calibrated x-ray fluorescence instrument to measure the weight of the metal per unit area of the coating (namely, in  $\mu\text{g}/\text{cm}^2$ ).

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The XRF Method makes the assumption that the metal film is as dense as its bulk form. With this assumption, the metal film's measured weight per unit area is then converted to a thickness in Angstroms, using its bulk density.

5 For completeness sake, it should be noted that sputtered metal films are often less dense than their corresponding bulk metals, so that above described assumption is not always precisely correct, and the XRF Method may in some cases underestimate the thickness of the metal film due to this  
10 variation in density. Thus, for the thin metal films, the initial measurement of weight per unit area ( $\mu\text{g}/\text{cm}^2$ ) is more accurate than the corresponding conversion to thickness based upon bulk density. Nonetheless, the XRF Method provides a useful approximation for comparing the relative thicknesses of  
15 the layers in coating.

In the following discussion, the thickness of the dielectric layers and/or films are given in ranges. As can be appreciated by those skilled in the art, the ranges are not limiting to the invention and the thickness may be selected to  
20 provide a coating stack of a desired color.

#### EXAMPLE 1

This Example 1 is Sample 1 of the Table 1. Sample 1 is a coated article that is shippable and heatable. The  
25 coating is a high transmittance, low emissivity coated article having a single infrared, reflective layer. Product having the coating stack of Sample 1 is made and the coating stack includes:

a clear glass substrate; a dielectric,  
30 antireflective layer deposited on the substrate, the layer includes (1) a zinc stannate film having 52 weight percent zinc and 48 weight percent tin (hereinafter referred to as 52-48 zinc stannate film) and having a thickness of  $260 \pm 40\text{\AA}$ , and  
(2) a zinc stannate film having 90 weight percent zinc and 10  
35 weight percent tin (hereinafter referred to as 90-10 zinc stannate film) and having a thickness of about  $80 \pm 45\text{\AA}$ ;

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a silver film having a thickness of about  $115 \pm 15\text{\AA}$  deposited on the 90-10 zinc stannate film,

a titanium primer film having a thickness of  $24-28\text{\AA}$  deposited on the metallic reflective film;

5 a dielectric, antireflective upper layer deposited on the titanium primer film, the dielectric, antireflective upper film includes a 52-48 zinc stannate film having a thickness of about  $230 \pm 60\text{\AA}$  deposited on the primer layer metal oxide, and

10 a titanium oxide layer having a thickness of  $36 \pm 7\text{\AA}$  deposited on the 52-48 zinc stannate layer or film.

#### EXAMPLE 2

This Example 2 is Sample 2 of the Table 1. The  
15 coated article has been made and is shippable and heatable with reduced haze. The coated article includes a glass substrate/a layer of a 52-48 zinc stannate film having a thickness of about  $230 \pm 40\text{\AA}$  and a zinc oxide film having a thickness of about  $80 \pm 40\text{\AA}$ ; a silver film having a thickness  
20 of  $110 \pm 10\text{\AA}$ ; a titanium metal primer film having a thickness of about  $18 - 23\text{\AA}$  and preferably  $19.5\text{\AA}$ ; a 52-48 zinc stannate film having a thickness of about  $820 \pm 40\text{\AA}$ ; a silver film having a thickness of about  $110 \pm 10\text{\AA}$ ; a metal primer having a thickness of about  $18 - 31\text{\AA}$  and preferably  $25\text{\AA}$ ; a 52-48 zinc  
25 stannate film having a thickness of about  $200 \pm 20\text{\AA}$ , and a titanium film having a thickness of about  $29 \pm 3\text{\AA}$ .

#### EXAMPLE 3

This Example 3 is Sample 3 of the Table 1. The  
30 coated article was not made; however, the following coated article is expected to be shippable and heatable with reduced haze. Example 3 includes a clear glass substrate; a dielectric, antireflective base layer deposited on the substrate includes a 52-48 zinc stannate film having a  
35 thickness of about  $310 \pm 20\text{\AA}$  deposited on the glass substrate; a first silver film having a thickness of about  $110 \pm 10\text{\AA}$

deposited on the 52-48 zinc stannate film; a first titanium primer film having a thickness of 18-29Å deposited on the first silver film; a dielectric, antireflective intermediate layer deposited on the first primer film, the intermediate  
5 layer includes a zinc oxide film having a thickness of  $80 \pm 40\text{\AA}$  deposited on the first primer film, a 52-48 zinc stannate film having a thickness of  $740 \pm 40\text{\AA}$  deposited on the zinc oxide film; a second silver film having a thickness of about  $110 \pm 10\text{\AA}$  deposited on the 52-48 zinc stannate film of the  
10 intermediate layer; a second titanium primer film having a thickness of about 18-31Å deposited on the second silver film; a dielectric, antireflective upper layer deposited on the second primer film, the dielectric upper layer is a 52-48 zinc stannate film having a thickness of about  $200 \pm 20\text{\AA}$ ; and a  
15 titanium metal protective film having a thickness of about  $29 \pm 3\text{\AA}$ , deposited on the 52-48 zinc stannate film of the dielectric upper layer.

#### EXAMPLE 4

20 This Example 4 is Sample 4 of the Table 1. The coated article of Example 4 was made and is shippable and heatable with the heated, coated article having reduced haze. The coated article of this Example 4 includes a clear glass substrate; a 52-48 zinc stannate film having a thickness of  
25  $310 \pm 20\text{\AA}$  deposited on the glass substrate; a first silver film having a thickness of  $110 \pm 10\text{\AA}$  deposited on the 52-48 zinc stannate film; a first titanium primer having a thickness of 18-29Å and preferably 22.5Å deposited on the first silver film; a 52-48 zinc stannate film having a thickness of about  
30  $820 \pm 40\text{\AA}$  deposited on the first titanium film; a second silver film having a thickness of about  $110 \pm 10\text{\AA}$  deposited on the 52-48 zinc stannate film; a second titanium film having a thickness of 18-32Å and preferably 21.5Å is deposited on the second silver layer; a zinc oxide film having a thickness of  
35  $80 \pm 40\text{\AA}$  deposited on the second titanium primer layer; a 52-48 zinc stannate film having a thickness of  $120 \pm 40\text{\AA}$  deposited on

the zinc oxide film and a titanium overcoat film having a thickness of  $29 \pm 3\text{\AA}$  over the 52-48 zinc stannate film.

#### EXAMPLE 5

5           This Example 5 is Sample 5 of the Table 1. The coated article was not made; however, it is expected that the coated article is suitable for shipment and heat treatment with the heated, coated article having reduced haze. The coated article of this Example 5 includes the films and layers  
10 similar to Example 3 except Sample 5 has a 52-48 zinc stannate film having a thickness of about  $230 \pm 40\text{\AA}$  deposited on the substrate and a zinc oxide film having a thickness of about  $80 \pm 40\text{\AA}$  deposited on the 52-48 zinc stannate film. The first titanium primer film on the first silver layer has a thickness  
15 of about  $18-29\text{\AA}$ ; the second titanium primer film on the second silver layer has a thickness of about  $18-31\text{\AA}$ . The remaining layers of Sample 5 are as shown in the Table and have the same composition and thickness for the same films as described in Example 3.

20

#### EXAMPLE 6

          This Example 6 is Sample 6 of the Table 1 and was made and is shippable and heatable with the heated, coated article having reduced haze. The coated stack is similar to  
25 the coating stack of Example 2 except a zinc oxide film having a thickness of about  $80 \pm 40\text{\AA}$  is deposited on the second titanium primer and a 52-48 zinc stannate film having a thickness of  $120 \pm 40\text{\AA}$  is deposited on the zinc oxide film. The first titanium primer layer had a thickness of  $19-26\text{\AA}$  and  
30 preferably  $19.5\text{\AA}$ , and the second primer layer had a thickness of  $21.5-31\text{\AA}$  and preferably  $25\text{\AA}$ . The composition and thickness of the remaining films/layers for Example 6 as shown for Sample 6 in the Table are as described in Example 2.

35

#### EXAMPLE 7

          This Example 7 is Sample 7 of the Table 1 and was made and is shippable and heatable with the heated coating

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stack having reduced haze. The coating stack of Sample 7 is similar to the coating stack of Example 3 except a zinc oxide film having a thickness of about  $80 \pm 40\text{\AA}$  was deposited on the second titanium film and a 52-48 zinc stannate film was deposited on the zinc oxide film. The first titanium primer layer had a thickness of about  $22-26\text{\AA}$  and preferably  $22.5\text{\AA}$ , and the second titanium primer layer had a thickness of about  $18-25\text{\AA}$  and preferably  $21.5\text{\AA}$ . The composition and thickness of the remaining films/layers for Example 7 as shown for Sample 7 on the Table are as described in Example 2.

#### EXAMPLE 8

This Example 8 is Sample 8 of the Table. The coated article was made and is a coated article suitable for shipment and heat treatment with the heated coated articles having reduced haze. The coated article of this Example 8 is a coated stack deposited on a clear glass substrate. The coating thickness and order of the films is as follows with film 1 deposited on the glass substrate.

#### TABLE 2

Film No. from Table	Composition of the Film	Thickness of the Film
1	52-48 zinc stannate	$230 \pm 40\text{\AA}$
2	zinc oxide	$80 \pm 40\text{\AA}$
3	1 <sup>st</sup> silver	$110 \pm 30\text{\AA}$
4	1 <sup>st</sup> titanium primer	$17-26\text{\AA}$ , preferably $19.5\text{\AA}$
5	zinc oxide	$80 \pm 40\text{\AA}$
6	52-48 zinc stannate	$740 \pm 40\text{\AA}$
8	2 <sup>nd</sup> silver film	$110 \pm 30\text{\AA}$
9	2 <sup>nd</sup> titanium primer	$18-31\text{\AA}$ , preferably $28\text{\AA}$
10	zinc oxide	$80 \pm 40\text{\AA}$
11	52-48 zinc stannate	$120 \pm 40\text{\AA}$
12	titanium metal overcoat	$29 \pm 3\text{\AA}$

The coated glass having the above coating was used in the fabrication of automotive windshields. The coated glass was cut to size, heated to shape the coated glass, and thereafter laminated to another shaped glass to provide an automotive windshield. The transmittance of the laminate was

greater than 70%, and reflects infrared energy. The windshield was made as is known in the art. Coated glass for use in automotive windshield was also made substituting 90-10 zinc stannate for the zinc oxide film. The coated article had  
5 film thickness in the ranges recited on Table 2.

As can be appreciated, the thickness of the primer layers presented in Table 2 can vary depending on cathode and sputtering equipment. For example, a shippable and heatable coating stack with reduced haze was made with a first titanium  
10 primer film having a thickness of  $18 \pm 0.5\text{\AA}$  and the second titanium primer film having a thickness of  $22 \pm 1\text{\AA}$

#### EXAMPLE 9

This Example 9 is Sample 9 of the Table and is a  
15 coated article that was made. The coated article was shippable and heatable with the heated, coated article having reduced haze. The coated article of this Example 9 is a coated stack deposited on a clear glass substrate. The coating thickness and order of the films is as follows with  
20 film 1 deposited on the glass substrate.

TABLE 3

Film No. from Table	Composition of the Film	Thickness of the Film
1	52-48 zinc stannate	$230 \pm 40\text{\AA}$
2	90-10 zinc stannate	$80 \pm 40\text{\AA}$
3	1 <sup>st</sup> silver	$107 \pm 30\text{\AA}$
4	1 <sup>st</sup> titanium primer	17-24Å, preferably 21.5Å
5	90-10 zinc stannate	$80 \pm 40\text{\AA}$
6	52-48 zinc stannate	$600 \pm 100\text{\AA}$
7	90-10 zinc stannate	$80 \pm 30\text{\AA}$
8	2 <sup>nd</sup> silver	$127 \pm 30\text{\AA}$
9	titanium metal primer	20-26Å, preferably 22.5Å
10	90-10 zinc stannate	$80 \pm 40\text{\AA}$
11	52-48 zinc stannate	$160 \pm 60\text{\AA}$
12	titanium oxide overcoat	$45 \pm 15\text{\AA}$

As can now be appreciated, a 90-10 zinc stannate  
25 film, a zinc oxide film and a zinc oxide, tin oxide film may be interchanged with one another and substituted for one another to obtain coated articles that are shippable and

heatable with reduced haze. However, in the practice of the invention the 9-10 zinc stannate film is preferred.

#### EXAMPLES 10-11

5           Examples 10 and 11 are Samples 10 and 11 of the Table. These examples were similar to example 9 with the following exceptions. For Example 10 titanium metal was the overcoat and for Example 11 titanium metal and titanium oxide were the overcoats. Example 11 was conducted in an  
10 alternative manner where the protective layer was first the titanium oxide film with the titanium film over top of it.

As can be appreciated, the thickness of the films is not limiting to the invention and may be selected to provide a coated article of a desired color as is known in the art.  
15 Further, the films of all examples of the invention may be interchanged to attain the features of the invention. A complete discussion of heating the coated glass sheets to automotive windshields, residential and commercial windows and other transparencies was not given as such technology is known  
20 in the art and as can now be appreciated used in the practice of the invention.

The invention is not limited to the examples presented above and that various changes and alterations can be made without departing from the spirit and broader aspects  
25 of the invention, as defined by the claims set forth below and by the range of equivalency allowed by law.



## WHAT IS CLAIMED IS:

1. An infrared reflective coated article comprising:
  - a substrate;
  - 5 a dielectric layer sputter deposited over the substrate, the layer comprising a first zinc stannate film deposited over the substrate having zinc in weight percent range of equal to and greater than 10 and equal to and less than 90, and tin in the weight percent range of equal to and  
10 less than 90 and equal to and greater than 10, and an electrical enhancing film deposited over the zinc stannate film, the electrical enhancing film selected from the group of films consisting of zinc oxide, tin oxide film and a second zinc stannate film wherein the composition of the first zinc  
15 stannate film is at least about 5 weight percent different than the composition of the second zinc stannate film, and an infrared reflective layer deposited on the dielectric layer,  
a metal primer layer over the infrared reflective  
20 layer;
  - a second dielectric layer over the primer layer; and  
a protective layer of at least two films selected from metal-containing and/or silicon-containing films selected from: metal and/or silicon and metal-oxy and/or  
25 silicon oxy-materials where the oxy materials are selected from oxides and oxynitrides and where the metal is the same or different and selected from a transition metal of Group , 4, 5, 6 or 10 of the Periodic Table of Elements.  
30
2. The coated article of claim 1 wherein the infrared reflective metal is silver and the silver is deposited on the zinc oxide, tin oxide film.
- 35 3. The article stack of claim 1 wherein the infrared reflective layer is a silver film and the silver film is deposited on the second zinc stannate film.

4. The article stack of claim 1 wherein the dielectric layer is a first dielectric layer and the infrared reflective layer is a first infrared reflective layer and  
5 further including:

a metal primer layer over the first infrared reflective layer;

a second dielectric layer over the primer layer and the protective layer is a overcoat over the second dielectric  
10 layer.

5. The article of claim 4 wherein the second dielectric layer is a zinc stannate film having 10-90 weight percent zinc and 90-10 weight percent tin.  
15

6. The article of claim 1 wherein the dielectric layer is a first dielectric layer and the infrared reflective layer is a first infrared reflective layer and further including:

20 a first metal primer layer over the first infrared reflective metal layer;

a second dielectric layer including over the first primer layer;

25 a second infrared reflective layer over the second dielectric layer;

a second metal primer layer over the second infrared reflective layer;

a third dielectric layer including over the second metal primer layer; and

30 the protective layer is over the third dielectric layer.

7. The article of claim 6 wherein at least one of the second and third dielectric layers includes a zinc  
35 stannate film having 10-90 weight percent zinc and 90-10 weight percent tin.

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8. The coating stack of claim 1 wherein the dielectric layer is a first dielectric layer and the infrared reflective layer is a first infrared reflective layer and further including:

5 a first metal primer layer over the first reflective layer;

a second dielectric layer over the first metal primer layer, the second dielectric layer comprising a first dielectric film and a zinc stannate film defined as a first  
10 zinc stannate film, the first zinc stannate film having zinc in the weight percent range of equal to and greater than 10 and equal to and less than 90 and tin in the weight percent range of equal to and greater than 10 and equal to and less than 90, the first dielectric layer deposited over the first  
15 metal primer layer;

a second infrared reflective layer deposited over the second dielectric layer;

a second metal primer layer deposited over the second infrared reflective layer;

20 a third dielectric layer deposited over the second primer layer; and

the protective layer is over the third dielectric layer.

25 9. The coating stack of claim 8 wherein the first dielectric film of the second dielectric layer comprises a zinc oxide film; a zinc oxide, tin oxide film or a zinc stannate film defined as a second zinc stannate film, the second zinc stannate film having a composition different than  
30 the composition of the first zinc stannate film of the second dielectric layer.

10. The coating stack of claim 9 wherein the second zinc stannate film of the second dielectric layer has  
35 zinc in the weight percent range of equal to and greater than 60 and equal to and less than 90 and tin in the weight percent

of equal to and greater than 10 and equal to and less than 40, and the third dielectric layer is a zinc stannate film.

11. The coating stack of claim 1 wherein the  
5 dielectric layer is a first dielectric layer and the infrared reflective layer is a first infrared reflective layer and further including:

a first metal primer layer over the first reflective layer;

10 a second dielectric layer over the first metal primer film;

a second infrared reflective layer over the second dielectric layer;

15 a second metal primer layer over the second infrared reflecting metal layer;

a third dielectric layer over the second metal primer layer, the third dielectric layer comprising a first dielectric film and a zinc stannate film defined as a first zinc stannate film, the first zinc stannate film having zinc  
20 in a weight percent with the range of equal to and greater than 10 and equal to and less than 90 and tin within the weight percent range of equal to and less than 90 and equal to and greater than 10, the third dielectric film deposited over the second metal primer; and

25 the protective layer overlies the third dielectric film.

12. The article of claim 11 wherein the first dielectric film of the third dielectric layer is selected from  
30 the group consisting of a zinc oxide film; a zinc oxide, tin oxide film or a zinc stannate film defined as a second zinc stannate film, the second zinc stannate film having a composition different than the composition of the first zinc stannate film of third dielectric layer.

35

13. The article of claim 12 wherein the second zinc stannate film of the third dielectric layer has zinc in

the weight percent range of equal to and greater than 60 and equal to and less than 90 and tin in the weight percent range of equal to and greater than 10 and equal to and less than 40.

5           14. The article of claim 1 wherein the dielectric layer is a first dielectric layer and the infrared reflective layer is a first infrared reflective layer and further including:

10                 a first metal primer layer over the first reflective layer;

                  a second dielectric layer over the first metal primer layer, the second dielectric layer comprising a first dielectric film and a zinc stannate film defined as a first zinc stannate film, the first zinc stannate film having zinc  
15                 in a weight percent within the range of equal to and greater than 10 and equal to and less than 90 and tin within the weight percent range of equal to and less than 90 and equal to and greater than 10, the second dielectric layer deposited over the first metal primer layer;

20                 a second infrared reflective layer over the first zinc stannate film of the second dielectric layer;

                  a second metal primer layer over the second infrared reflective layer;

                  a third dielectric layer over the second metal  
25                 primer layer, the third dielectric layer comprising a first dielectric film and a zinc stannate film defined as a first zinc stannate film, the first zinc stannate film having zinc in a weight percent within the range of equal to and greater than 10 and equal to and less than 90 and tin within the  
30                 weight percent range of equal to and less than 90 and equal to and greater than 10, the third dielectric layer deposited over the second metal primer layer; and

                  the protective layer overlies the first zinc stannate film of the dielectric layer.

35

                  15. The coating stack of claim 14 wherein the first dielectric film of the second dielectric layer and the

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first dielectric film of the third dielectric layer each has a film selected from the group consisting of zinc oxide film; zinc oxide, tin oxide film or second zinc stannate film having a composition different than the composition of the first zinc  
5 stannate film in the respective same second or third dielectric layer.

16. The coating stack of claim 15 wherein the second zinc stannate film of the first and second dielectric  
10 layer each include zinc in the weight percent range of equal to and greater than 60 and equal to and less than 90 and tin in the weight percent of equal to and greater than 10 and equal to and less than 40.

15 17. The coating stack of claim 14 wherein the second dielectric layer further includes a third dielectric film over the first zinc stannate film of the second dielectric layer.

20 18. The coating stack of claim 15 wherein the second dielectric layer further includes a third dielectric film over the first zinc stannate film of the second dielectric layer wherein the third dielectric film of the second dielectric layer is a film selected from the group  
25 consisting of zinc oxide film, zinc oxide, tin oxide film and a zinc stannate film defined as a third zinc stannate film, the third zinc stannate film has a composition different than the composition of the zinc stannate film of the second dielectric layer closest to the third zinc stannate film.

30 19. The coating of claim 15 wherein the second dielectric film of the second dielectric layer and the second dielectric film of the third dielectric second layer each comprises a zinc oxide film; a zinc oxide, tin oxide film or a  
35 second zinc stannate film having a composition different than the composition of the first zinc stannate film of third dielectric layer.

20. The coating stack of claim 19 wherein the first and third dielectric films of the second dielectric layer and the first dielectric film of the third dielectric layer each include zinc in the weight percent range of equal to and greater than 60 and equal to and less than 90 and tin in the weight percent of equal to and greater than 10 and equal to and less than 40.

21. The coating stack of claim 17 wherein the second zinc stannate film of the first dielectric layer is on the glass piece and has a thickness in the range of  $230 \pm 40$  Angstroms Å; the first zinc stannate film of the first dielectric layer is on the second zinc stannate film of the first dielectric layer and has a thickness in the range of  $80 \pm 40$  Å; the first infrared reflective metal layer is a first silver film deposited on the first zinc stannate film of the first dielectric layer and has a thickness in the range of  $110 \pm 30$  Å, the metal primer layer is a titanium film deposited on the first silver layer and has a thickness in the range of  $17 - 26$  Å; the first dielectric film of the second dielectric layer is deposited on the titanium film and has a thickness in the range of  $80 \pm 40$  Å; the first zinc stannate film of the second dielectric layer is deposited on the first dielectric film of the second dielectric layer and has a thickness in the range of  $740 \pm 40$  Å; the second infrared reflective metal layer is a second silver film deposited on the second dielectric film of the second dielectric layer and has a thickness in the range of  $110 \pm 38$  Å; the second primer film is a titanium film deposited on the second silver layer and having a thickness in the range of  $18 - 31$  Å; the first dielectric film of the third dielectric layer is deposited on the second titanium film and has a thickness in the range of  $80 \pm 40$  Å; the first zinc stannate layer of the third dielectric layer is deposited on the first dielectric film of the third dielectric layer and has a thickness in the range of  $120 \pm 40$  Å, and the protective layer is a titanium metal film deposited on the first zinc

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stannate layer of the third dielectric layer and has a thickness in the range of  $29 \pm 3\text{\AA}$ .

22. The coating stack of claim 1 wherein the  
5 protective layer has at least two films selected from a metal of titanium, zirconium, niobium, tantalum, chromium, nickel and alloys thereof, and a metal oxy material selected from: titanium oxides, titanium oxynitride, zirconium oxides, zirconium oxynitrides, niobium oxides, niobium oxynitrides,  
10 tantalum oxide, tantalum oxynitride, chromic oxides, chromic oxynitrides, nickel oxide, nickel oxynitride, silicon oxide, silicon dioxide, silicon aluminum nitride and combinations or mixtures of any two or more of these, where either the silicon, metal or the metal oxy material is the first film of  
15 the layer.

23. A coated article comprising:  
a substrate;  
a first dielectric layer over the substrate;  
20 a first infrared reflective layer over the first dielectric layer;  
a first metal primer layer over the first infrared reflective layer;  
a second dielectric layer over the first metal primer, the  
25 second dielectric layer having a first dielectric film selected from the group consisting of zinc oxide, tin oxide film and a first zinc stannate film, and a second dielectric film the second dielectric film having a composition different than the first dielectric film of the second dielectric layer;  
30 a second infrared reflective layer over the second dielectric layer;  
a second primer layer over the second reflective layer;  
a third dielectric layer over the second metal  
35 primer layer; and



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a protective layer of at least two films selected from metal-containing and/or silicon-containing films selected from: metal and/or silicon and metal-oxy and or silicon oxy-materials where the oxy materials are selected from oxides and  
5 oxynitrides and where the metal is the same or different and selected from a transition metal of Group , 4, 5, 6 or 10 of the Periodic Table of Elements..

24. The coated article of claim 23 wherein the  
10 first dielectric layer includes a zinc stannate film, the second dielectric film of the second dielectric layer is a zinc stannate film and the third dielectric layer includes a zinc stannate film, each of the zinc stannate films having zinc in the weight percent range of 10-90 and tin in the  
15 weight percent range of 90-10.

25. The coated article of claim 24 wherein the first dielectric film of the second dielectric layer is the first zinc stannate film having zinc in the weight percent  
20 range of equal to and greater than 90 and equal to and less than 60 and tin in the weight percent range of equal to and greater than 10 and equal to and less than 40.

26. A coated article comprising:  
25 a substrate;  
a first dielectric layer over the substrate;  
a first infrared reflective layer over the first dielectric layer;  
a first metal primer layer over the first infrared  
30 reflective layer;  
a second dielectric layer over the first metal primer layer;  
a second infrared reflective layer over the second dielectric layer;  
35 a second metal primer layer over the second reflective metal layer;

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a third dielectric layer having a first dielectric film selected from the group consisting of zinc oxide film; zinc oxide, tin oxide film; a first zinc stannate film and a second dielectric film overlying the first dielectric film, 5 the second dielectric film having a composition different from the first dielectric film; and

the protective layer overlying the third dielectric layer where the protective layer is at least two films selected from metal-containing and/or silicon-containing films 10 selected from: metal and/or silicon and metal-oxy and or silicon oxy-materials where the oxy materials are selected from oxides and oxynitrides and where the metal is the same or different and selected from a transition metal of Group , 4, 5, 6 or 10 of the Periodic Table of Elements.

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27. The coated article of claim 26 wherein the first and second dielectric layers are each a zinc stannate film, and the second dielectric film of the third dielectric layer is a zinc stannate film and each of the zinc stannate 20 films has zinc in the weight percent range of 10-90 and tin in the weight percent range of 90-10.

28. The coated article of claim 27 wherein the first dielectric film of the second dielectric layer has zinc 25 in the weight percent range of equal to and greater than 90 and equal to and less than 60 and tin in the weight percent range of equal to and greater than 10 and equal to and less than 40.

30

29. A coated article comprising:

a substrate;

a first dielectric layer over the substrate;

a first infrared reflective layer over the first dielectric layer;

35

a first primer layer over the first reflective metal layer;

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a second dielectric layer having a first dielectric film selected from the group consisting of zinc oxide, tin oxide film and a first zinc stannate film, and a second dielectric film overlying the first dielectric film having a composition different than the first dielectric film of the second dielectric layer;

a second infrared reflective layer over the second dielectric layer;

a second primer layer over the second reflective layer;

a third dielectric layer over the second metal primer layer, the third dielectric layer having a first dielectric film selected from the group consisting of a zinc oxide, tin oxide film and a first zinc stannate film and a second dielectric film, the second dielectric film of the third dielectric layer have a composition different than the composition of the second dielectric film of the third dielectric layer; and

the protective layer overlying the third dielectric layer where the protective layer is at least two films selected from metal-containing and/or silicon-containing films selected from: metal and/or silicon and metal-oxy and or silicon oxy-materials where the oxy materials are selected from oxides and oxynitrides and where the metal is the same or different and selected from a transition metal of Group , 4, 5, 6 or 10 of the Periodic Table of Elements..

30. The coated article of claim 31 wherein the first dielectric layer, the second dielectric film of the second and third dielectric layers are each a zinc stannate film having zinc in the weight percent range of 10-90 and tin in the weight percent range of 90-10.

31. The coated article of claim 32 wherein the first dielectric film of the second and third dielectric layers are each a zinc stannate film having zinc in the weight percent range of equal to and greater than 90 and equal to and

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less than 60 and tin in the weight percent range of equal to and greater than 10 and equal to and less than 40.

34. The coated article of claim 32 wherein the  
5 coated article is a transparency.

35. The coated article of claim 34 wherein the  
coated article is an automotive transparency.

10 36. The coated article of claim 35 wherein the  
automobile transparency is an automotive windshield having a  
pair of glass sheets laminated together and one of the sheets  
is fabricated from the substrate having the coating.

15 37. A method of making an automobile transparency  
comprising:

applying a coating on a glass substrate having the  
following:

20 a first dielectric layer over a glass substrate;  
a first infrared reflecting metal layer over the  
first dielectric film:  
a first metal primer layer over the first reflective  
layer;  
a second dielectric layer over the first metal  
25 primer layer;  
a second infrared reflective layer over the second  
dielectric layer;  
a second metal primer layer over the second infrared  
reflective layer;  
30 a protective layer overlying the first zinc stannate  
film of the third dielectric layer where the protective layer  
is at least two films selected from metal-containing and/or  
silicon-containing films selected from: metal and/or silicon  
and metal-oxy and or silicon oxy-materials where the oxy-  
35 materials are selected from oxides and oxynitrides and where  
the metal is the same or different and selected from a

transition metal of Group , 4, 5, 6 or 10 of the Periodic Table of Elements.,

wherein at least one of the dielectric layers includes a first dielectric film selected from the group consisting of zinc  
5 oxide, tin oxide and a first zinc stannate film and a second dielectric film including a second zinc stannate film having a composition different than the first zinc stannate film and a composition of 10-90 weight percent zinc and 90-10 weight percent tin;

10 processing the coated substrate to provide a coated windshield blank wherein the processing step includes heating the coated substrate to its bending temperature and after heating the coating has reduced haze;

laminating the coated blank to another piece of  
15 glass to provide the automobile windshield.

38. A coated article comprising:

a substrate;

at least one dielectric layer over the substrate;

20 at least one infrared reflective layer over the first dielectric layer;

optionally a first metal primer layer over the first infrared reflective layer;

optionally a second dielectric layer over a first  
25 metal primer; and

at least one protective layer selected from (A) a heat convertible metal film wherein the metal is selected from titanium, zirconium, niobium, tantalum, chromium, nickel and alloys thereof and alloys with silicon, (B) at least two films  
30 selected from metal-containing and/or silicon-containing films selected from: metal and/or silicon and metal-oxy and or silicon oxy-materials where the oxy materials are selected from oxides and oxynitrides and where the metal is the same or different and selected from a transition metal of Group , 4,  
35 5, 6 or 10 of the Periodic Table of Elements, wherein the protective layer is located in the stack of layers to provide chemical and/or mechanical durability to the stack of layers.

39. A coated article of Claim 38 wherein the dielectric layer is a first dielectric layer and the infrared reflective layer is a first infrared reflective layer and further  
5 including:

a second infrared reflective layer over the second dielectric layer;

optionally a primer layer over the second infrared reflective layer

10 a second dielectric layer over the primer layer; and  
the protective layer is an overcoat over the second dielectric layer.

40. A coated article of Claim 38 wherein the protective  
15 layer is a heat convertible metal located on the substrate before the first dielectric layer.

41. A coated article of Claim 38 wherein the protective layer is a heat convertible metal located on the  
20 substrate before the first dielectric layer.

42. A coated article of Claim 38 wherein the protective layer is a heat convertible metal located between the first dielectric layer and the second dielectric layer below the  
25 first reflective layer.

43. A coated article of Claim 39 wherein the protective layer has at least two films in either order of metal or silicon and metal oxy material or silicon oxy material located between the  
30 second dielectric layer on the reflective layer and a third dielectric layer.

44. A coated article of Claim 1, wherein the protective layer has a thickness for the films of about 5 to about 60 Å  
35 for the metal or silicon film and about 20 to about 50 Å, for the oxy-material film.

45. A coated article of Claim 44, wherein the protective layer has a thickness for the films of 10 to about 30 Å for the metal or silicon film and 30 to 40 Å for the oxy-material film.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/15576

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C03C17/36 C23C14/34

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C03C C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 803 481 A (PPG INDUSTRIES INC) 29 October 1997 (1997-10-29) cited in the application column 10, line 6 - line 40 column 26, line 40 - line 51	1-45
X	GB 2 311 540 A (GLAVERBEL) 1 October 1997 (1997-10-01) claims 27-33; tables A,B	1-45
X	US 4 902 580 A (GILLERY F HOWARD) 20 February 1990 (1990-02-20) column 4, line 27 -column 5, line 58	37-45
X	US 5 059 295 A (FINLEY JAMES J) 22 October 1991 (1991-10-22) the whole document	37-45
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Int l Application No  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 99 58736 A (PPG IND OHIO INC) 18 November 1999 (1999-11-18) cited in the application page 13, line 12 - line 22; claims <u>        </u>	1-45

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/15576

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0803481	A	29-10-1997	US 5821001 A	13-10-1998
			AU 701514 B	28-01-1999
			AU 1903297 A	30-10-1997
			CA 2200093 A	25-10-1997
			JP 10034794 A	10-02-1998
			KR 215380 B	16-08-1999
			US 5942338 A	24-08-1999
GB 2311540	A	01-10-1997	BE 1011440 A	07-09-1999
			CZ 9700888 A	14-01-1998
			DE 19712527 A	06-11-1997
			ES 2134717 A	01-10-1999
			FR 2746791 A	03-10-1997
			IT T0970216 A	18-09-1998
			JP 10024515 A	27-01-1998
			PL 319150 A	29-09-1997
			PT 101981 A, B	30-09-1997
			SE 9701075 A	27-09-1997
			US 6090481 A	18-07-2000
US 4902580	A	20-02-1990	US 4834857 A	30-05-1989
			AT 101588 T	15-03-1994
			AU 3232189 A	05-10-1989
			CA 1335887 A	13-06-1995
			CN 1037550 A, B	29-11-1989
			DE 68913068 D	24-03-1994
			DE 68913068 T	07-07-1994
			DK 157189 A	02-10-1989
			EP 0339274 A	02-11-1989
			ES 2051316 T	16-06-1994
			FI 891527 A	02-10-1989
			HK 1006834 A	19-03-1999
			JP 2009731 A	12-01-1990
			JP 2505276 B	05-06-1996
			KR 9205470 B	04-07-1992
			NO 302901 B	04-05-1998
			NZ 228159 A	29-01-1991
			ZA 8901665 A	28-11-1990
US 5059295	A	22-10-1991	US 4806220 A	21-02-1989
			AT 77808 T	15-07-1992
			BR 8707076 A	02-08-1988
			CA 1331867 A	06-09-1994
			CN 87105971 A, B	31-08-1988
			DE 3780148 A	06-08-1992
			DE 3780148 T	24-12-1992
			EP 0275474 A	27-07-1988
			ES 2032807 T	01-03-1993
			GR 3005637 T	07-06-1993
			JP 8336923 A	24-12-1996
			JP 7015143 B	22-02-1995
			JP 63183164 A	28-07-1988
			KR 9101774 B	23-03-1991
			US 4898790 A	06-02-1990
			US 5270517 A	14-12-1993
WO 9958736	A	18-11-1999	AU 3972699 A	29-11-1999